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Viscosity Dependence of the Rates of Diffusional Processes

David L. Weaver

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pressures (using Curle's theory), and Mach number dependencies agree with wind tunnel experiments. A double pressure peak is found in the model (credited to image action) which is qualitatively similar to measured

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Viscosity Dependence of the Rates of Diffusional Processes

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INTRODUCTION

Systems which are overdamped due to the frictional drag of solvent have the motion of their constituents described by the diffusion equation as an approximation to the Fokker-Planck equation (1). Because of the frequent occurrence of this condition, diffusional models are commonly used to describe biological, physical and chemical processes including heat conduction, mass transport, some aspects of chemical reactions, and so on. In order to apply the general diffusion equation to a particular physical situation or model, the space in which diffusion occurs must be designated and the behavior of appropriate combinations of the particle density and its derivatives specified at the boundaries. However, in the physical situation in which there is partial or complete absorption (capture or reaction depending on the particular problem being modeled) at the boundary, it has not been completely clear how to interpret the parameters determining the boundary condition. In Ref. 2 in the context of the diffusion-collision model of protein folding, two possible parameter choices were discussed in detail and a third possibility, the one to be outlined below in the present paper, was mentioned without proof. Since the third possibility leads to the rates of diffusion-controlled processes having a solvent viscosity-independent part as well as a viscosity-dependent part, it has important consequences for intramolecular and intermolecular movements in biological systems. In addition, recent numerical studies (3) and approximate analytical calculations (4) on one-dimensional diffusional systems have lent credence to the third possibility. Therefore, the purpose of the present paper is to present a derivation of the "radiation" or partially absorbing boundary condition (the perfect absorber being a special case) for a diffusion-controlled process in which not every collision

between a Brownian particle and the absorbing boundary results in removal of the particle from the diffusion space. The details of the derivation are follwed by a discussion of some experiments involving intramolecular polypeptide movements in which the solvent viscosity was varied, and the implications for diffusion in membranes in which localization due to trapping takes place (5,6).

THE DERIVATION

To be specific, one-dimensional diffusion will be discussed below. The designation of the space determines whether the system is infinite or finite, and in the latter case one must specify the length of the space in order to calculate quantities of physical interest in absolute terms.

Consider finite space diffusion first (infinite space diffusion will be considered later). Boundary conditions must be specified at two boundaries, $x = a$ and $x = b$ with $b > a$. Let the particle density be $\rho(x,t)$ at position x and time t. The diffusion equation is

$$\frac{\partial \rho}{\partial t} = D\frac{\partial^2 \rho}{\partial x^2} \qquad a < x < b \tag{1}$$

with D the diffusion coefficient (assumed constant). The boundary conditions at a and b, which along with the initial value $\rho(x,o)$ are needed to specify $\rho(x,t)$, are to be linear combinations of ρ and its first derivatives $\partial\rho/\partial x$ and $\partial\rho/\partial t$. In the absence of particle emission at the boundaries, $\partial\rho/\partial t$ will not contribute to the boundary conditions. Since the particle flux is $\vec{\partial}(x,t) = -D\partial\rho/\partial x\ \hat{x}$, which is the net number of particles per second crossing a unit area perpendicular to the x-axis,

a completely reflecting boundary at which no absorption takes place is uniquely specified by the condition $\vec{\partial} = 0$. Let this boundary condition prevail at $x = b$ in the one-dimensional finite space example. Thus, $\partial\rho/\partial x = 0$ at $x = b$.

At the boundary $x = a$, let the conditions be such that partial absorption takes place. That is, some fraction of the Brownian particles that reach the boundary at $x = a$ are not reflected and no longer diffuse. This general case encompasses the limits of perfect absorption and perfect reflection as well as all intermediate situations. For partial absorption, the reflected flux at $x = a$ will be smaller than the incident flux by the number of particles per second being absorbed, that is $\partial_+ = \gamma\partial_-$, $0 \leq \gamma \leq 1$, where ∂_- is the magnitude of the flux toward the boundary at $x = a$ and ∂_+ is the magnitude of the reflected flux at $x = a$ (that is, the portion of the net flux at $x = a$ going in the positive x direction). In the spirit of kinetic theory, one may write $\partial_\pm(a,t) = \langle v\rangle_\pm \rho_\pm(a,t)$ where $\rho_\pm(a,t)$ are the reflected (+) and incident (-) particle densities and $\langle v\rangle_\pm$ are "average" values for the reflected and incident particle velocities at $x = a$ derived from the mean value theorem of the calculus. If the absorption mechanism at the boundary is independent of velocity, then $\langle v\rangle_+ = \langle v\rangle_- = \langle v\rangle$. This will be assumed as the simplest possibility. In many situations the boundary will be due to a potential energy barrier whose height sets a minimum value for the kinetic energy of the incident particles in order to be absorbed at $x = a$. Nevertheless, if the approach to a Maxwell-Boltzmann velocity distribution is fast on the diffusion time scale,

then the incident and reflected particle velocity distributions will be virtually identical. Then, since

$$\partial(a,t) = \partial_+(a,t) - \partial_-(a,t) = (\gamma - 1)\langle v\rangle \rho_-(a,t) \tag{2}$$

and

$$\rho(a,t) = \rho_+(a,t) + \rho_-(a,t) = (1 + \gamma)\rho_-(a,t) \tag{3}$$

one obtains the boundary condition

$$\partial(a,t) = \frac{-(1 - \gamma)}{(1 + \gamma)} \langle v\rangle \rho(a,t) \tag{4}$$

or

$$\left.\frac{\partial \rho}{\partial x}\right|_a = \frac{(1 - \gamma)}{(1 + \gamma)} \frac{\langle v\rangle}{D} \left.\rho\right|_a \tag{5}$$

Note that with this boundary condition, perfect absorption $\gamma = 0$ does not imply $\rho|_a = 0$. However, for perfect reflection $\gamma = 1$, the condition $\partial\rho/\partial x|_a = 0$ is found. The consequence of Eq. (5) for several biophysical situations have been briefly mentioned by the present author previously (2,6,7) without discussion. Below some of the implications and relevant experiments are analyzed.

THE IMPLICATIONS

Eq. (5) has important implications about the rates of some diffusional processes. The rates of absorption in the model outlined above may be calculated using an extension of the idea of first passage times (8), as shown by a number of authors (9,10,11). This is carried out below for the diffusional model considered above by writing the fraction of particles absorbed at x = a in terms of the mean absorption time (inverse of the absorption rate.

Let the fraction of absorbed particles be $n_a(t)$, so that

$$n_a(t) = 1 - \int_a^b dx\ \rho(x,t) \tag{6}$$

where ρ is normalized initially to one particle (thus, ρ may be thought of as the relative position probability density). Solution of the diffusion equation with the given boundary conditions and an initial distribution in which the particles start at $x = b$ indicates that the infinite series of decreasing exponential terms which represents the time dependence of $n_a(t)$ may be well-approximated by a single exponential. That is,

$$n_a(t) \tilde{=} 1 - \exp(-t/\tau) \tag{7}$$

with

$$\tau = \frac{(b-a)^2}{2D} + \frac{(b-a)}{\langle v \rangle}\ \frac{(1+\gamma)}{(1-\gamma)} \tag{8}$$

If the initial particle distribution is uniform rather than concentrated at $x = b$, Eq. (8) is modified slightly be the replacement of 2 by 3 in the first term.

Two points are indicated by Eq. (8). First, that a measurement of the inverse rate should show a linear dependence on solvent viscosity (via D) plus a viscosity independent term (the other forms of Eq. (5) which are commonly used (2) would have both terms in Eq. (8) being proportional to D^{-1}). Second, that a perfect absorber ($\gamma = 0$) has a viscosity independent term, which can complicate the use of diffusion measurements to find D (see below). As mentioned in Refs. 3 and 4, the $\gamma = 0$ perfect absorber situation does not (using Eq. (5)) lead to $\rho|_a = 0$ as the boundary condition. It does, however, lead to the boundary condition $\rho(x,t) = 0$ at $x = a - \Delta$, $\Delta > 0$ where Δ is a length parameter (referred to as the Milne extrapolation length) whose value is

$$\Delta = \frac{(1+\gamma)}{(1-\gamma)} \frac{D}{\langle v \rangle} \tag{9}$$

Eq. (9) was found by computing the rate of particle injection at x = b needed to have the above diffusional model at steady-state with one particle in the region (a,b) in order to compare with the results of Refs. 3 and 4. This comparison also allows one to more precisely identify <v> to be $(\alpha/2)^{\frac{1}{2}}$ where $\alpha \equiv k_B T/m$ with k_B the Boltzmann constant, T the absolute temperature and m the Brownian particle mass. Note that α is the mean square velocity in one-dimension for a Maxwell-Boltzmann distribution. Another interpretation is $\langle v \rangle = v_M/2$ where v_M is the most probable speed.

SOME RELEVANT EXPERIMENTS

The "radiation" boundary condition derived above leads to the possibility that the rates of diffusion driven processes may not be directly proportional to D and, in fact, may be effectively independent of D for small enough γ. In this regard, some experiments have been carried out to study the intramolecular motion of polypeptide chain segments in solvents of different viscosities (since, according to the Einstein relation $D = k_B T/f$ with f the friction coefficient, varying the viscosity ought to vary D in an inverse manner). Haas et al. (12) investigated the kinetics of the fluorescence decay of the energy donor in a homologous series of oligopeptides, each containing at its ends a donor and an acceptor of electronic excitation decay energy in solvent mixtures of different viscosities. With an assumed theoretical analysis, diffusion coefficients were derived which increased systematically upon decreasing

the solvent viscosity. The values obtained for the diffusion coefficients were about an order-of-magnitude smaller than the values expected for the diffusion coefficients of the free chromophores in solvents of comparable viscosity, and appear to have a solvent viscosity independent part in the derived values of D^{-1}. Although the results obtained for D in this experiment are probably model dependent, there is a clear dependence of diffusion coefficient on solvent viscosity, as well as the suggestion of a viscosity independent contribution to D^{-1}. In the analysis of this experiment the boundary condition $\rho(a,t) = 0$ was used rather than Eq. (5) with $\gamma = 0$.

Tsong and Baldwin (13), on the other hand, in their study of the kinetics of folding of the two forms of unfolded ribonuclease A (with all disulfide bonds intact) as a function of solvent viscosity, by adding either sucrose or glycerol, found no dependence on solvent viscosity, the rates of the two observed reactions being either unchanged or slightly faster in the presence of sucrose or glycerol. In the same system, Tsong (14) has recently found a reaction which is strongly dependent on solvent viscosity and somewaht faster than the reactions observed in Ref. 13.

The precise interpretation of these experimental results is not completely clear, at present, due to the complexity of the systems involved. However, it appears that diffusion mediated reactions are playing a signfiicant role, and that there are both solvent viscosity dependent and solvent viscosity independent contributions to the kinetics, perhaps of the kind suggested by Eq. (8) and the subsequent discussion.

If one assumes that considerations similar to those leading to Eq. (5) apply also to the two-dimensional surface of membranes, then

localization in such systems due to diffusion-driven trapping (5,6) will also show the mixed dependence on D of Eq. (8),although the detailed form will be different (see Ref. 6). In that case, D would not be simply directly proportional to the localization rate. This problem requires further study. Some approximate results have been obtained by Harris (15) for the related problem of steady absorption of Brownian particles by an infinite right circular cylinder, corresponding to absorption by a circular sink in two dimensions. A modified boundary condition was again found by introducing an effective radius of absorption corresponding to the Milne extrapolation length in one-dimension.

The extension of the above ideas to infinite systems leads to further interesting results concerning approach to equilibrium effects. Consider, as a definite example, a spherically symmetrical infinite system of molecules of initial uniform concentration ρ_o surrounding a target of radius a centered at r = o. The molecules diffuse in the infinite space, and their concentration as a function of position and time, $\rho(r,t)$ satisfies the diffusion equation, Eq. (1), within the limits $a < r < \infty$. Corresponding to Eq. (5), the boundary condition appropriate to the infinite space is

$$aL \left.\frac{\partial \rho}{\partial r}\right|_a = \rho|_a \tag{10}$$

where aL will be the three-dimensional analog of $(1 + \gamma)D/((1 - \gamma)\langle v\rangle)$ in Eq. (5). As $r \to \infty$, $\rho(r,t) \to \rho_o$ for the other boundary condition.

The above diffusion problem may be solved, in principle, using the Laplace transform method to obtain $4\pi a^2 D \left.\frac{\partial \rho}{\partial r}\right|_a$, the time dependent rate of association. To proceed further, suppose that the initial

concentration of targets is equal to ρ_0 also. Then, the theory of von Smoluchowski (16) for colloidal particles may be applied here to yield $n_a(t)$ the probability that a target molecule pair is formed before time t. The result is

$$n_a(t) = \frac{(t/[(1 + L)T])}{1 + (t/[(1+L)T])} \tag{11}$$

where $T \equiv 1/(4\pi a D \rho_0)$, the "unit" of time appropriate to this physical situation. Again, there appears a mixed D dependence in the overall rate of association. Harris (17) has recently studied numerically the related problem of steady-state absorption by a sphere.

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16. Abstract

It is shown that the rates of diffusion-controlled processes may have a solvent viscosity independent part as well as a viscosity dependent part. Some relevant experiments involving intramolecular polypeptide movements are discussed, and implications for some experiments on diffusion in membranes are outlined.

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